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Stability of a new geopolymer grout: Rheological and mechanical performances of metakaolin-fly ash binary mixtures

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HIGHLIGHTS

- Alkali-activated grout mixtures were designed using metakaolin, fly ash, and xanthan gum.
- Rheological behaviour influenced by the viscosity of the solution and the packing density of powders.
- Evolution of elastic modulus combined with isothermal calorimetry to monitor setting and hardening.
- Strength and volume stability affected by increasing fly ash proportion.

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ABSTRACT

The evolution of technical and environmental requirements fosters the development of geopolymer based grouts for soil reinforcement. Geopolymer based materials actually have several advantages but the improvement of their rheological performances remains a challenging task, as the raw materials, especially sodium silicate and metakaolin, do not have favorable properties and the main chemical admixtures used to optimize cement-based materials have not been found compatible. As mix-design takes into account the performances in both fresh and hardened states, a comprehensive study is necessary to develop geopolymer grouts based on metakaolin-fly ash-stabilizer mixtures. Fly ash allowed reducing the viscosity and increasing the setting time and the stabilizer provided the fresh mixes with better homogeneity and stability. At constant liquid to solid ratio, the packing density of the powders actually increases with fly ash proportion. Fly ash affected the mechanical properties, especially at replacement rates of 40% and higher, due to combined effects of reduced reactivity and higher packing density of the powders. This could be shown by a new methodology combining the monitoring the elastic properties with isothermal calorimetry for understanding the early-age behavior and the distinction between the geopolymerization stages. The addition of xanthan gum had a beneficial effect on the stability of grouts, by acting on the activation solution without having any significant effect on the geopolymerization reaction.

1. Introduction

Geopolymers can be obtained by the activation of a raw material usually in the form of a powder, under the action of a solution at high pH and in the presence of a solution of soluble alkali silicates [1]. These raw materials may be of natural or industrial origins. In general, any raw material rich in silicon and aluminum readily soluble by the action of an alkaline activator represents a good candidate for the process of geopolymerization, the latter is known by its exothermic character. The exact mechanism of the geopolymerization reaction is still unknown due to the rapidity of the reaction as well as the simultaneity of its steps, but most of the research works agree on three stages: dissolution of the aluminosilicate source to enrich the medium with reactive precursors of the reaction, polycondensation allowing a restructuring and a rearrangement towards a more stable state of these precursors which lead to the formation of a so-called gel phase. The last step is the hardening of the gel phase [2]. The nomenclature uses three types of linear oligomers called polysialates of empirical formula

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$M_n[(SiO_2)_z\ AlO_2]_n \cdot wH_2O$ The structure of these oligomers depends on the value of z (z = Si/Al), n is the degree of polymerization, M is alkali metal ion (generally sodium or potassium) [3]. Due to the variety of available raw materials, activation, and environmental conditions, the actual composition of formed materials is likely to change significantly and not to be pure geopolymer. In this paper the terms *geopolymer* or *geopolymerization* refer to materials including geopolymer phases and not only to the geopolymer gel.

From an environmental point of view, the development of geopolymers can be considered as an activity with a relatively low negative environmental impact due to its lower processing energy and carbon footprint in comparison with conventional materials. Geopolymerization can occur under mild conditions and is considered a cleaner process because of the lower CO_2 emissions than those from cement production [4,5]. The diversity of possible raw materials makes waste and by-products of some industries the source of reactive species necessary for the geopolymerization reaction such as blast furnace slag and fly ash. The latter are residues in the form of fine particles which come from some energy-intensive industries, usually in coal-fired power plants. They are captured in the combustion gases by electrostatic or by filtration before the flue gases reach the chimneys [6].

Fly ash is classified according to its composition, generally rich in SiO_2, Al_2O_3, CaO and Fe_2O_3, and presented in a form of amorphous and crystalline oxides or various minerals. Their aluminate and silicate contents make fly ashes, particularly class F ash, good candidates for geopolymerization reactions [1]. These reactions are affected by several factors, namely the nature of the raw materials and their crystallinity [7–9]. It is accepted that the higher the content of amorphous phases, the greater their reactivity. Among these factors, the type and the concentration of the alkaline activator are also indicated [10,11]. At a high pH, a better dissolution of the sources of the aluminate species and silicate occurs. SiO_2 / Al_2O_3 and solid/liquid ratios have an important effect on the rheology in the fresh state and mechanical performances in the hardened state [12,13]. Curing conditions also play a very important role in improving the properties of geopolymers and have an influence on their durability [14]. Resistance to chloride, sulphate, acid and efflorescence is closely related to the microstructure and the transport properties of the material. These can be adjusted by controlling the activation solution and the curing conditions [15,16]. For the binary metakaolin-fly ash geopolymer mixtures (which will be called "MK-FA geopolymers" along this section), the curing temperature and the concentration of the NaOH solution can be optimized in order to achieve optimum mechanical properties [10].

MK-FA geopolymers can be used in various conditions for the adsorption and immobilization of toxic metals [4], or in applications requiring thermal and thermo-physical properties such as thermal conductivity and resistance of high temperatures and fire. It has been shown that the introduction of fly-ash into metakaolin-based geopolymers considerably improves the fire resistance compared to a geopolymer based only on metakaolin [17]. The use of geopolymer MK-FA mixtures in civil engineering increased, due to the availability of fly ash and, on the other hand, to the performance approved by specialists [18,19]. Activated slag and metakaolin-based materials show good reactivity and allow reaching high strength, however it is often intended to delay setting, which can be achieved by the use of MK-FA or slag-fly ash mixtures [20]. Moreover the availability of fly ash and slag is limited by the associated industrial productions [21] , thus it is better to combine these products with natural raw materials such as metakaolin, which is produced from the calcination of kaolinite-rich clay [22]. Mortars based on NaOH-activated MK-FA mixtures exhibited remarkable sensitivity to elaboration conditions, as chemical changes in alkaline activators had a significant impact on initial strength with higher molarity [13]. Previous study on MK and MK-FA geopolymers including ^{29}Si and ^{27}Al NMR data and mechanical characterization showed that MK-FA geopolymers remained very stable in terms of reaction products and macroscopic properties [23].

The injection of cement grout is widely used in many soil treatment applications to improve or restore their mechanical and hydraulic properties, but very few studies deal with the geopolymer grouts in the literature [24]. It is necessary that grouts easily penetrate into the medium to be strengthened, but they must also ensure good stability of the material in the fresh as well as hardened state. Although the mix-design and behavior of MK-FA geopolymers has already been investigated [20], a comprehensive study including the engineering properties that matter for injection grouts, and analyses of the microstructure, cannot be found.

So as to study the feasibility of the injection of geopolymers, a compromise between the fluidity and the stability of the grout must be taken into consideration. In relatively diluted mixtures, the mineral particles tend to sediment under the effect of gravity, which results in remarkable heterogeneity. This affects long-term structural behavior, thus it is essential to control the homogeneity of the material during its production. Increasing the viscosity of the suspending fluid in suspensions with low dry matter content, particularly grout, is necessary to ensure a satisfactory state of stability, but the viscosity under injection conditions, i.e. at higher shear rates, must be as low as possible [25]. Therefore, for cementitious grouts, bentonite is the most commonly used material in diluted grouts.

To our knowledge, very few works have been carried out on the addition of polysaccharide-based viscosity modifying admixture in the preparation of geopolymer mixtures, in particular xanthan gum. The characteristic properties of the latter in aqueous solutions lead to suspensions with important rheological properties. Although xanthan gum is widely used in the food industry, it is also used in civil engineering applications, as the pseudo plasticity of xanthan gum optimizes the viscosity of mixtures (mortars) and ensures their good hold after projection and before drying [26].

The present work is a contribution to answer questions about the role that viscosity modifying agents can play as an additive to improve the stability of geopolymer-based grouts and its possible effect in geopolymerization reactions. In this paper, we present the results of the study of the stabilization of a geopolymer grout based on a binary metakaolin-fly ash mixture. This study combines non-standardized tests and standardized tests showing the influence of fly-ash proportion, and the effects of a stabilizing additive on the properties of the grouts in both fresh and hardened states.

2. Materials and methods

2.1. Materials

The design of the geopolymer grouts of the present study required the use of dry materials and aqueous solutions. Technical products were used. The appropriate amount of sodium hydroxide was added to a commercially available sodium silicate solution (Table 1) to prepare the activation solution. The dry powders are composed of metakaolin from Fumel, France and fly ash from Hornaing, France.

Dry powders were characterized by several methods. Mineralogical analysis was conducted by X-ray diffraction (Bruker AXSD4, Cu $K\alpha = 0.154$ nm). Differential thermal and gravimetric analysis (DTA / TGA) was carried out using (TG-DTA / DSC Labsys) instrument, operating in a temperature range from 25 °C to 1250 °C with 10 °C/min heating rate. Particle size of powders analysis was carried out using submicron particle sizer NICOMP 380, distilled water was used as a dispersant of particles.